

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Improvements in Methods of Treating Metallic Pieces.

We, OFFICE NATIONAL D'ETUDES ET DE RECHERCHES AERONAUTIQUES, O.N.E.R.A., a Body Corporate organised and existing under the laws of France, of 25, Avenue de la Division Leclerc, CHATILLON-SOUS-BAGNEUX (Seine), France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is aimed at the production of metallic pieces which are required to undergo at least one thermal treatment (comprising heating to a temperature of from 700 to 1500°C.), followed by rapid cooling or quenching, but which are to have, when the production is finished, a non oxidized superficial layer.

To this end, in accordance with this invention, the piece concerned is heated to a high temperature in a substantially neutral or reducing atmosphere containing at least one fluorine compound and is cooled without passing through an atmosphere of a nature other than that above specified.

By the method according to this invention we ensure that no oxide layer is formed on the piece treated during the high temperature heating treatment, such oxide layer being stable and very difficult to remove. Although slight oxidation might occur during the subsequent quenching treatment if an oxidising medium, e.g. water, is used for quenching, such oxidation is readily removable, e.g. by an electrolytic treatment.

Our invention is particularly concerned with the treatment of metallic pieces provided at their surface with a layer of an alloy of the metal of the piece with at least one other metal (in particular chromium), hereinafter called "addition metal," this superficial layer of alloy being obtained by diffusion of the addition metal into the piece and being hereinafter referred to as a "diffusion superficial layer."

[Price 3s. 6d.]

The treatment to produce diffusion of the addition metal into the superficial layer of the piece includes heating at relatively high temperature and generally this heating will destroy the existing physical and mechanical properties of the piece, and it is usual to subject the piece to a rapid cooling or quenching to improve the properties.

In accordance, therefore, with a feature of this invention, as applied to metallic pieces provided in this way with a diffusion superficial layer, the said rapid cooling or quenching is performed immediately after said superficial diffusion treatment, that is to say when the piece is still substantially within the temperature range of the diffusion operation.

Other features of the invention are set out in the claims hereto.

Preferred embodiments of our invention will be hereinafter described with reference to the accompanying drawings, given merely by way of example, and in which:

Figs. 1 and 2 diagrammatically show in section two systems for treating pieces according to different embodiments of our invention,

Figs. 3 and 4 are axial sections of two hollow pieces having stressed skins and made according to the present invention, and

Fig. 5 diagrammatically shows in axial section a chromizing furnace for carrying out the treatment of a metallic wire according to our invention.

We shall examine the case of a method for obtaining metallic pieces (for instance ferrous pieces) provided with a diffusion superficial layer of at least one addition metal (for instance chromium), when said superficial layer is obtained by a treatment taking place at a temperature and for such a time that the physical and mechanical properties of the pieces are modified.

In this case, the chromizing treatment above referred to is first carried out, this treatment being performed, in a manner which is known in itself, in a fluorine containing atmosphere,

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whereby the addition metal is transferred onto the pieces by a fluoride of said addition metal, the treatment temperature being advantageously about 1000-1100°C., that is to say within a range favourable to the formation of a chromized layer but in which a substantial modification of the physical and mechanical properties of the pieces generally takes place.

The physical and mechanical properties of the ferrous pieces which have been lost during the chromizing treatment are improved by subjecting them to a quenching treatment, either after they have been heated to the optimum temperature for quenching in a neutral or reducing atmosphere containing a fluorine compound, or immediately after the chromizing treatment in a fluorine compound atmosphere (that is to say when said pieces are at a temperature little different from those required for chromizing).

This quenching treatment may be carried out in direct fashion, that is to say by immersing the pieces in a liquid which achieves a strong cooling thereof, said liquid being either a non oxidizing liquid (for instance oil), or an oxidizing liquid (for instance water).

Another possibility, particularly useful where quenching should not be so intensive, consists in subjecting the pieces to an indirect quenching by immersion, not of the pieces proper, but of substantially fluidtight boxes, preferably the boxes in which said pieces have undergone the chromizing treatment.

Our invention is particularly advantageous if care is taken, not only to subject the pieces to a treatment for improving their physical and mechanical properties, but to maintain the superficial state (brightness) which has been given thereto by the chromizing treatment. In such a case, the pieces remain, in the course of their cooling and insofar as they are not directly immersed in a cooling liquid, in contact with a neutral atmosphere to which has been added at least one fluorine compound, which atmosphere may advantageously, in the case of chromized pieces, be the very atmosphere which has been used for the chromizing treatment.

We thus avoid, owing to the presence of this fluorine compound, the slight oxidizing which would necessarily take place in a so-called neutral or reducing atmosphere obtained from industrial gases (hydrogen or ammonia for instance) which always contain traces of an oxidizing substance sufficient for tarnishing the bright ferrous surfaces.

The above-mentioned treatments have a particular importance when the pieces chromized in a fluorine containing atmosphere contain substantial amounts of carbon and are therefore liable to have, after quenching, satisfactory physical and mechanical characteristics.

Steel pieces containing amounts of carbon greater than 0.2% may in fact carry either

thick layers rich in chromium and of a great brightness, if the treatment has been preceded or accompanied by a superficial decarburizing, or very thin layers, containing chiefly chromium carbide, very hard and of dull appearance, if steps have been taken in the course of the treatment to avoid decarburizing of the pieces.

Concerning this point, the following explanations are given as to the nature of the superficial layers of some chromized pieces.

In the case of ferrous pieces containing a substantial amount of carbon, it is possible to obtain thick and protective diffusion layers of ferro-chromium by subjecting these pieces at the beginning of the operation (or during a preliminary operation) to sweeping by moist hydrogen at a temperature ranging from 700 to 950°C. It is also possible superficially to decarburize the pieces by adding to the reaction mass water or ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ ). These steps may be taken whenever the pieces contain a relatively high proportion of carbon. Good results may also be obtained by superficially oxidising the pieces for some time before the chromizing operation. The iron oxides that are formed start being reduced during the diffusion operation at temperatures averaging 500°C with the formation of water vapour which produces a superficial decarburizing of steel in the presence of hydrogen.

The above mentioned treatments may also apply to steels containing a high proportion of carbon and containing for instance tungsten and for which chromizing has produced a considerable superficial hardening resulting from the formation of a continuous superficial layer of chromium carbide. The diffusion of chromium is accompanied by an enrichment of the superficial steel layers in carbon at the cost of the underlying layers. There is formed a very hard chromium carbide layer which opposes a deep penetration of chromium. It should be indicated that if such a hard chromizing is desired, it may be interesting to reduce the decarburizing effect of the sweeping gases by reducing the volume of the active atmosphere owing to the use of powders to surround the pieces as above described.

Such a hard chromizing treatment may be applied to steels which contain only from 0.2 to 0.3% of carbon, but in this case any decarburizing is to be avoided. For this purpose, it is advantageous to increase the proportion of ammonium fluoride in the atmosphere, to use only anhydrous products and to treat pieces which have been perfectly deoxidised. This is necessary because oxides are reduced only at temperatures ranging from 400 to 800°C, i.e. at temperatures where the formation of water would have a very strong decarburizing action.

It should be noted that since the superficial

layer consisting chiefly of chromium carbide is little liable to melt, there are few risks of superficial adhesion by intersolid diffusion. It is therefore possible to operate as well with a method in which the pieces are in contact with the cementation mixture as with a method in which the operation takes place in gaseous phase. The best method seems however to be the so-called semi-contact gaseous phase method, according to which the pieces, insulated from the reaction mass, are in contact with a mass of the addition metal (chromium) preferably surrounded by an inert diluting body such as zirconia or alumina (the diluting body reduces the volume of the gaseous atmosphere which may accidentally have a decarburizing effect).

The temperature of the chromizing treatments depends upon the nature of the pieces:

Phosphorus pig iron is generally treated at temperatures ranging from 875 to 900°C, and steel containing from 0.4 to 0.6 of carbon is covered with a very hard protective coating of about 3/100 of a millimeter of chromium carbide after a treatment of two hours at 1075°C in an atmosphere of chromium fluoride and hydrogen.

Fig. 1 shows a device for carrying out a heating treatment of pieces having undergone chromizing after which heating said pieces are directly quenched in a liquid. In the case of pieces having undergone a hard chromizing, the treatment box 1 is closed at its upper part and a removable bottom 2 gives it a substantial fluidtightness. As a matter of fact, it seems preferable in this case to form the fluorine containing reducing atmosphere by introducing into the treatment box fluorine containing compounds, advantageously a very volatile fluoride such as ammonium fluoride and a slightly volatile fluoride such as chromium fluoride. This last mentioned fluoride, after evaporation of the first mentioned one, exerts a sweeping action and maintains, during the whole of the treatment, a fluorine containing reducing atmosphere. But we may also use other fluorides such as nickel or aluminium fluoride. We may advantageously add small amounts of the addition metal (chromium) if the temperature from which quenching is carried out is to exceed 1050°C.

Thus, for instance, we may introduce an amount of ammonium fluoride ranging from fifty grams to a fraction of a gram per liter and about 10 times less of chromium fluoride, the latter being placed out of contact with the pieces.

If the heating which takes place before quenching is effected at temperatures ranging from 800 to 900°C, there is practically no chromizing. The atmosphere contains a relatively low amount of active fluoride; the temperature is too low for substantial chromizing and the pieces remain only for a

short time at the maximum temperature. It is then unnecessary to provide a reserve of chromium in the treatment chamber because there are practically no losses due to chromium diffusion into said pieces.

We will now describe an example in which needle valve screws and pivots of measurement apparatus (steel containing 0.5% of C) having undergone a hard chromizing treatment were treated to improve their initial physical and mechanical qualities. In this example, the pieces had been covered with a very hard superficial layer of chromium carbide very resistant to wear and tear (up to 1200-1500 Vickers). The mechanical qualities of the metal mass had been considerably reduced by the chromizing treatment but they were improved by a heating at 975°C in the above stated conditions (i.e. in a neutral or reducing atmosphere containing chromium fluoride vapours), followed by an oil quenching without the pieces being allowed to pass through an atmosphere other than that above mentioned. Pieces were obtained having no wear and tear or deformation after passage on a vibrating table.

In order to avoid any contact with air when the pieces are dropped into vessel 3, which contains the quenching liquid, which consists of water mixed with oil or fluorine, we provide a jacket 4 which extends downwardly from the furnace to the vessel, box 1 being fixed in a detachable manner to said jacket, for instance by means of pins 5 the removal of which enables said box to drop into the vessel, whereby the pieces can be directly immersed in the liquid by opening of the removable bottom.

A slight modification may be provided in the device shown by Figure 1 if it is desired to improve the mechanical qualities of pieces having superficial thick and bright chromized layers. The pieces are placed in bulk inside the box. The bottom 2 of this box is provided with orifices for the passage of gases. Box 1 is provided with a tube at its upper part, through which we circulate in the box a continuous current of hydrogen enriched with fluorine containing compounds, for instance by passing this hydrogen at a temperature higher than 500° on chromium impregnated with chromium fluoride. This chromium impregnated with chromium fluoride may be obtained for instance from a reserve of chromium which has been impregnated with chromium fluoride with condensation thereof in the course of chromizing operations proper. It is advantageously placed in the upper part of the box.

We chromized furnace fire-bars and steel mazout burners of a carbon steel containing 2% of carbon by a treatment of eight hours at a temperature of 1080°C, so as to obtain a diffusion layer 0.25 mm thick. According to our invention these pieces were subjected to

or reducing atmosphere containing compounds of fluorine and they were quenched by dropping them directly from this atmosphere into an oil quenching bath.

After several hundreds of hours in an atmosphere which is sometimes reducing, sometimes oxidizing, in combustion gases which sometimes contain sulphur, only an insignificant scaling was found on the fire-bars without any penetration of corrosion along the joints of the grains.

If an intensive quenching is desired, the pieces may be dropped into salt water for instance, advantageously containing ammonium fluoride, but in this case the pieces which drop into the quenching liquid at a temperature higher than  $900^{\circ}\text{C}$  may be slightly oxidised. In order to eliminate this very fine and very stable chromium oxide formed while the pieces are immersed in said quenching liquid, the pieces may subsequently be treated electrolytically. We then use the pieces as cathodes in an electrolyte formed of a molten mixture of soda and of sodium or potassium carbonate. The operation takes place at a temperature of  $275\text{--}400^{\circ}\text{C}$  which does not substantially modify the physical and mechanical properties of the pieces. The operation lasts from several seconds to several minutes. Advantageously we make use of a voltage of 4-6 volts with a current density of 0.1-0.5 amperes per sq. cm.

If the quenching treatment is carried out at a temperature lower than  $875/900^{\circ}\text{C}$ , or if, at a higher temperature, ammonium fluoride is added to the quenching water, it often suffices, in order to eliminate the oxide, to proceed to a short electrolytic treatment.

Thus, it is possible to chromize chain elements in the rough state made of carbon steel containing 0.25% of C by a superficially decarburizing treatment. After chromizing, the chain is formed and it is subsequently heated at a temperature of  $875^{\circ}\text{C}$  in a neutral or reducing atmosphere containing chromium fluoride vapours, after which it is dropped directly from this atmosphere into water (to which ammonium fluoride may be added). In the same conditions, we treated springs and after the operation we proceeded to a reheating at  $350^{\circ}\text{C}$  for two hours and an electrolytic treatment for several seconds. In both cases, very good physical and mechanical characteristics were obtained.

During the cooling of chromized pieces (in particular of pieces made of the metal designated by the Registered Trade Mark Nimonic), a brittle superficial layer is formed. In the course of the chromizing treatment taking place for eight hours at  $1080^{\circ}\text{C}$  in a neutral or reducing atmosphere containing chromium fluoride vapours, the superficial zone is strongly enriched with chromium and

quenched. The chromium which has diffused in the metal of the piece at high temperature is generally less soluble at low temperature and a layer of compounds which are generally brittle may be formed in the course of cooling. This brittle layer is easily eliminated, according to a feature of our invention, by electrolytic treatment.

This electrolytic treatment might also permit the elimination of the brittle sigma phase if it existed in chromized ferrous pieces. But in the case of ferrous pieces, a quick quenching at the end of the chromizing treatment has in fact the advantage of avoiding the superficial formation of this sigma phase which is generally formed only in the course of a slow cooling and whose presence is undesirable.

If such a layer of sigma phase exists on pieces previously chromized it will be eliminated if, in a treatment according to our invention including a heating in a neutral or reducing atmosphere containing chromium fluoride vapours followed by a quick quenching, the heating treatment is conducted at a temperature above  $820^{\circ}\text{C}$ . This is due to the fact that the sigma phase does not exist at a temperature higher than  $820^{\circ}\text{C}$ .

Concerning now indirect quenching, that is to say an accelerated cooling obtained by direct drop, at the end of the operation, of the chromizing boxes into a quick quenching liquid such as water to which sodium chloride or calcium chloride has been added, it is of interest to make use of apparatus such that a reducing atmosphere surrounds the boxes. We also avoid any inflow of air or steam into the space where the reducing atmosphere is circulating (which space is constituted for instance by a bell-shaped furnace 6 as illustrated by Fig. 2) by placing, at the outlet of this space and above the quenching tank 3, a diaphragm 7 the maximum opening of which is just sufficient to enable the treatment box 1 to pass therethrough and in this case said box must be made liquidtight. The opening of this diaphragm makes it possible to control the drop of the box into the quenching liquid.

When operating in a continuous furnace, we spray with a cooling liquid the portions of the liquid tight boxes that project from a diaphragm similar to that of Fig. 2 when they leave the circulation conduit through which they are evacuated from the furnace.

Accelerated cooling makes it possible to reduce the total time required for the treatment and therefore to increase the efficiency of the furnaces.

It is even possible, according to another feature of our invention, further to reduce the time required for the treatment by cooling the pieces in an apparatus which has no con-

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nection with the treatment furnace, which can thus be immediately reloaded. In this case, a treatment box such as is removed from the furnace when it is still at a temperature higher than 500°C and placed in an independent apparatus where it is cooled in an atmosphere of hydrogen.

It should be noted that this feature of our invention may be applied generally to the transfer of relatively fluidtight boxes and it will suffice, in order to prevent this transfer from giving rise to an oxidizing of the pieces, to move them when they are still at a temperature at least equal to 500°C while taking care to maintain in said boxes a neutral or reducing atmosphere which contains fluorine compounds.

The rate of cooling of the pieces being substantially lower than that obtained by direct quenching in a liquid, it is advantageous, when it is desired to obtain the best possible mechanical characteristics, to make use of steels having a rate of hardening lower than the natural rate of cooling of the pieces in air (such steels containing active elements which delay transformation, such in particular as nickel and chromium). An example of composition of such a steel, which is well adapted to a chromizing treatment with accelerated cooling, is the following one: carbon 0.3/04%, nickel 4%, chromium 1.2%, silicon 0.3/04%, manganese 0.3/05%, with possible traces of boron, the remainder being iron and unavoidable impurities.

In addition to its application to the reheating of chromized steels or similar alloys, the brightening and reducing power of fluorine containing atmospheres may be applied in general to the treatment of any ferrous pieces and even of stainless steels or alloys; ferrous pieces can easily be reheated so as to make them bright by placing the pieces in bulk in a diluting body such as talcum with ammonium fluoride therein. The brightening of initially oxidized ferrous pieces may be explained by the fact that the iron oxide is transformed into iron fluoride at temperatures averaging 900°C with formation of water which is gradually eliminated according to the equations  $2\text{NH}_4\text{F} = 2\text{HF} + 3\text{H}_2 + \text{N}_2$ ,  $\text{Fe}_2\text{O}_3 + 4\text{HF} + \text{H}_2 = 2\text{FeF}_2 + 3\text{H}_2\text{O}$ . Subsequently, the iron fluoride thus formed is reduced according to the equation  $2\text{FeF}_2 + 2\text{H}_2 = 2\text{Fe} + 4\text{HF}$  and iron deposits on the piece which is thus covered with an iron film (thus cementing itself).

If it is desired to provide hollow metallic pieces having a thin stressed skin, it is possible to chromize a rough piece of corresponding shape, to improve by a thermal treatment as above described the physical and mechanical properties of this rough piece deteriorated by chromizing, and finally to eliminate by a chemical attack the internal portion of the piece which does not include chromium.

If furthermore, precautions have been taken to avoid any superficial oxidizing, e.g. by quenching in a non-oxidising medium, we finally obtain a piece having a thin and elastic wall, of uniform thickness, and having a bright superficial layer which is resistant to corrosion.

In this way, we obtained flexible tubes and aneroid diaphragms. The pieces were obtained from mild steel containing from 0.05 to 0.15 of carbon. They were machined externally, then chromized at a temperature of 1075°C. The duration of the chromization treatment was chosen so that the walls had the desired thickness. With a treatment of two hours, we obtained a thickness of about 0.12 mm. Cooling was obtained quickly by directly dropping a chromization box into salt water. After cutting off of the two ends by means of which the pieces were held, these pieces were hollowed out by means of boiling nitric acid. After this attack, we obtained a hollow piece P (Fig. 3) having the following properties: Satisfactory elasticity, a uniform thickness which can be easily predetermined, a perfect superficial finish and a high resistance to corrosion.

It is advantageous, in order to accelerate the acid attack, to provide at the centre of the rough piece a passage which is carefully protected against the active vapours during the chromization operation, which passage may for instance be constituted by a threaded bore sealed by means of two plugs 8 during chromizing.

It should be noted that it is possible, as shown by Fig. 4, to provide a single piece constituted by the juxtaposition of several identical pieces. These pieces are subsequently separated by cutting after chromizing.

Another example of chromizing followed by a thermal treatment for improving the physical and mechanical properties by controlled cooling is illustrated by Fig. 5 which relates to the continuous treatment of a metallic wire F.

This wire, wound off from a spool 13, passes with a continuous movement through a tube 14 provided with holes in its walls and surrounded by a charge of cementation mixture C (a mixture of, for instance, chromium and ammonium fluoride, capable of giving off, when heated, vapours of chromium fluoride) and of chromium R, said charge being contained inside a bell-shaped furnace. Sweeping by means of hydrogen is obtained through a conduit 15 and there is provided, in the top of the furnace, a spout 16 for the introduction of the reagents.

The central tubular conduit 14 extends to the outside of the furnace and constitutes a conduit 14a which passes through a cooling container 17. The chromized wire which issues from said extension 14a may undergo a final electrolytic treatment in a tank 18

before being wound up on a drum 19. Cooling (for instance by means of water) avoids the formation on the iron wire of a superficial layer of sigma phase which is brittle. As for the electrolytic treatment, it further improves the superficial qualities of the chromized wire.

It should be noted that it is of interest, with such a plant, to work at high temperature (for instance at a temperature of about 1150°C) in order to make it possible to work at a higher rate of unwinding. For instance, at this temperature, if the wire passes through the apparatus in five minutes, a diffusion layer of 0.02 mm. is obtained. For a time of thirty minutes, a layer ranging from 0.06 to 0.08 mm. is obtained, and for a time of one hour, a layer ranging from 0.1 to 0.12 mm.

If it is desired to improve the efficiency of the installation, we may dispose in parallel in the same space several tubes such as 14 for the simultaneous treatment of as many metallic wires.

What we claim is:

1. A method of producing a metallic piece which has to undergo at least one main thermal treatment, this treatment comprising a heating at a temperature ranging from 700 to 1500°C, followed by rapid cooling or quenching and which is to have, when its production is finished, a non oxidized superficial layer characterized in that said piece is heated to a high temperature in a substantially neutral or reducing atmosphere containing at least one fluorine compound and is cooled without passing through an atmosphere of a nature other than that above specified.

2. A method according to claim 1 in which said fluorine compound is a fluoride of an addition metal capable of diffusing into the metal of the piece, the heating being conducted in conditions, in particular of temperature, such that there is a diffusion of said addition metal into the superficial layer of the piece, characterized in that the said rapid cooling or quenching is performed immediately after said superficial diffusion treatment, that is to say when the piece is still substantially within the temperature range of the diffusion operation.

3. A method according to claim 2 in which the quenching operation is performed by direct immersion of the piece in a cooling liquid.

4. A method according to claim 1 in which the quenching operation is effected indirectly, by immersion in a liquid of a substantially fluidtight box containing the piece and in which the diffusion treatment has been carried out.

5. A method according to any of claims 2 to 4 further including an electrolytic treatment after the quenching treatment to eliminate any brittle superficial layer that may have been formed.

6. A method according to claim 1 in which the quenching operation is carried out after a reheating of the piece which has undergone a superficial diffusion treatment and a subsequent cooling.

7. A method according to claim 1 for obtaining of hollow pieces wherein a solid piece of an external shape corresponding substantially to that of the desired piece is subjected to a superficial diffusion treatment, after which the piece is hollowed out by a chemical attack on the metal of said piece but not the superficial diffusion layer, the quenching treatment being carried out before the piece is hollowed out.

8. A method according to claim 1 for obtaining of a metallic wire, for instance a ferrous one, to be superficially coated with a metallic diffusion layer, for instance of chromium, wherein this wire is passed in a continuous fashion through a tubular member in which there is an atmosphere of a fluorine compound of the addition metal intended to form this diffusion layer, the first portion of said tubular member being at a temperature capable of ensuring diffusion and the remainder being cooled down to the temperature necessary for improving the physical and mechanical properties of the wire.

9. A method of treating a metallic piece including a quick cooling or quenching piece substantially as hereinbefore described with reference to and as shown by Fig. 1, Fig. 2 or Fig. 5 of the accompanying drawings.

10. Metallic pieces when treated by the method of any of the preceding claims.

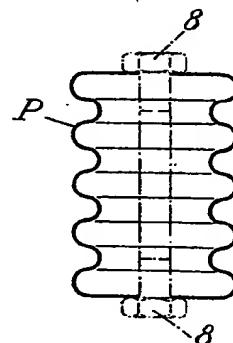
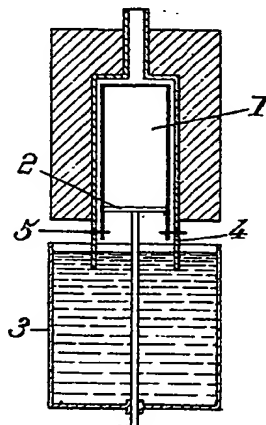
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*Fig. 1.*



*Fig. 4*

